

COATINGS. ENAMELS

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BINDING STRENGTH AND STRESS DECREASE IN POWDER MATERIAL – SILICATE COATING COMPOSITES

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The possibility of using silicate coatings as protection for bismuth-containing powder materials is considered for the purpose of expanding their service properties. A method for pretreatment of powder steel surface by borating before enameling is proposed, which makes it possible to obtain high adhesion strength in powder material – silicate coating composites.

Lately machine-building technology increasingly uses parts produced from powder materials. Their application areas expand, which involves the need for such parts to operate in different media. The problem of increasing wear, atmosphere, and corrosion resistance of such materials becomes topical. It is often more convenient and less expensive to solve this problem not by modifying the composition and properties of entire material, but by modifying only its surface. Obtaining respective coatings on the surface of powder materials is sufficient for imparting the required properties.

A promising line of research in this field, in our opinion, is the development of powder material – silicate coating composites, since silicate coatings, depending on their composition and structure, have a wide range of properties and sometimes surpass other types of coatings in their service characteristics.

To ensure reliable protection of powder products from corrosion, atmospheric, and temperature effects and to ensure enhanced surface hardness in order to decrease their wear in service, the authors set the aim of producing a high-quality silicate coating on powder steel.

It is known [1] that the quality of the silicate coating is achieved by ensuring optimum formation conditions, and the strength of adhesion of a coating to its substrate to a large extent depends on the correct selection of compositions, coordination of their thermal coefficients of linear expansion (TCLE), and the quality and properties of the surface to be coated, which can be controlled by preliminary treatment. Therefore, the silicate coatings selected by us for steel powder materials were standard undercoat and surface enamels

ÉSG-21, ÉSG-31, ÉSP-200^a, and ÉSP-210^b, which are capable of forming high-quality coatings on a metal substrate, and their different combinations can modify coating properties. The selection of the undercoat enamels is motivated by the fact that they contain adhesion oxides. The interest in using surface enamels as one-layer coatings, which in standard conditions have low adhesion to steel of grades 08kp and 10kp, is due to the fact that surface enamels have better service characteristics than undercoat enamels. The standard slip method was used for producing coatings.

The substrate was bismuth-bearing powder steel previously developed at the South Russia State Technical University [2], which can be easily cut and, therefore, makes it possible to produce high-precision machine parts. It was assumed that such materials would ensure high adhesion to silicate coatings, since bismuth in them is not chemically bonded to the main material and at a certain temperature can migrate to the surface of the product [2]. Oxidized at the temperature of coating formation, bismuth transforms into Bi₂O₃, which is capable of incorporating in the glass structure and, accordingly, has a positive effect on the strength of adhesion of enamel to powder material in the resulting composites.

The compliance of the TCLEs of silicate coating and powder steel has a great effect on durability and good adhesion strength [1]. To reveal compatibility of the TCLE of the substrate and silicate coating, the TCLE of powder materials used in the experiments (PZhV 2.160.26 and PZhR 2.200.28 with 1 wt.% bismuth additive) were calculated using the Appen method taking into account partial properties of all components comprising the powder steels investigated [1].

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The calculated TCLE values of bismuth-containing powder materials lie within an interval of $(136.8 - 137.4) \times 10^{-7} \text{ }^{\circ}\text{C}$ and virtually coincide with the TCLE of steel 08kp most frequently used for enameling ($136.5 \times 10^{-7} \text{ }^{\circ}\text{C}$). This made it possible to propose an effective solution for the problem of obtaining a high-quality powder material – silicate coating composite using standard silicate enamels used for enameling steel 08kp, which have the TCLE of $(96.3 - 102.1) \times 10^{-7} \text{ }^{\circ}\text{C}$.

For preliminary treatment of materials before applying coatings, we selected the method of low-temperature liquid borating in boron-containing solutions (RF Patent No. 2135631) [3], which is unusual for the silicate industry, but more environment-friendly than the commonly used degreasing and pickling methods. Borating powder steel samples was carried out in borax and boric acid solutions at 400°C using process activators. As a result of borating, a layer of iron borides Fe_3B , Fe_2B , and FeB was formed on the surface of powder materials. Furthermore, the presence of bismuth chemically not bonded to the matrix of the powder material also contributed to the modification of the powder steel surface under pretreatment. At the temperature of borating metal in solutions of boron-containing compounds bismuth diffuses toward the surface and in some places sweats out onto the surface of the samples, which later has a positive effect on the process of coating formation.

The selected standard enamels were deposited on pretreated powder-steel surface using the slip method, and coatings were formed at a temperature of $850 - 860^{\circ}\text{C}$. The obtained powder steel – silicate coating composites were analyzed for their adhesion and impact strength using methods developed at the South Russian Technical University [4]. The testing results demonstrated sufficiently high adhesion strength and impact strength both of coatings based on undercoat and on surface standard enamels.

The high strength parameters of surface enamels that do not contain adhesion oxides deposited on powder steel can be accounted for by complete reactions of iron borides with enamel melt in the course of the coating formation. As a result, the iron from the borides forms iron silicates $2\text{FeO} \cdot \text{SiO}_2$ facilitating adhesion, and boron incorporates into the glass structure forming $[\text{BO}_4]^{5-}$ complexes and strengthening it.

Furthermore, good strength of adhesion of a silicate coating to bismuth-containing powder materials can be facilitated by the composition and structure of powder steel itself, which differs from compact steel in its residual porosity promoting mechanical adhesion, and in the presence of oxide impurities (MnO , SiO_2 , P_2O_5 , etc.), which may enter in reactions with the glass matrix of the coating.

It is known [5] that powder materials oxidize more intensely than compact steels, which may result in formation of an excessive quantity of iron oxides on the substrate surface at the stage of silicate coating sintering and later lead to decreasing adhesion strength and even to peeling of the coating along its transitional layer. The presence of a bismuth film,

which sweats out on powder steels considered under elevated temperatures, prevents excessive oxidation of metal surface [2]. Pure bismuth at this temperature reacts with atmospheric oxygen and form bismuth oxide Bi_2O_3 . Bismuth oxide, in turn, is capable of incorporating in the structure of the vitreous phase of enamel [6], thus facilitating an increase in the strength of adhesion in the bismuth-bearing powder material – silicate coating composite.

Electron-microscope studies of the composites obtained revealed the presence of a transitional layer on the powder steel – enamel interface, which is formed as a consequence of reactions of bismuth film and iron oxide on the surface of the powder material with the furnace atmosphere and enamel melt. Owing to its specific composition (presence of $2\text{FeO} \cdot \text{SiO}_2$ and bismuth-borosilicate composite), the transitional layer decreases the residual stresses arising inevitably in the course of coating formation, which strengthens the powder steel – silicate coating system.

Thus, as a consequence of the reaction of iron borides with enamel melt and atmospheric oxygen dissolved in it, complexes $[\text{BO}_4]^{5-}$ incorporate into the structure of the vitreous phase of the transitional layer act as a buffer and reduce stresses in the powder steel – silicate coating composite.

Usual stresses (caused by a difference in TCLE) inevitably arise in a powder material – silicate coating composite produced by the standard slip method: compressive stresses in the coating layer and tensile stresses in the powder steel layer. An excess of these stresses may decrease the strength of the composite. However, the presence of bismuth in the powder material layer has a positive effect on relaxation of arising stresses. Thus, the presence of 1 wt.% bismuth in powder steel increases its plasticity and relative elongation [2], which is due to bismuth-initiated accommodation processes in relay deformation transfer between individual system elements. Furthermore, the presence of bismuth oxide, which had reacted with the enamel melt in the transitional layer, raises to some extent the TCLE of the bismuth-borosilicate composite and brings it closer to the TCLE of powder steel. All this leads to a positive effect of bismuth on stress relaxation in the powder steel – silicate coating composite.

The composites obtained were tested for acid resistance by a fast method, i.e., the spot sample method [4, 5]. Composites based on surface enamels have higher acid resistance than composites based on undercoat enamels. Analysis of alkali and water resistance revealed similar satisfactory results in both composites. The increase in acid, alkali, and water resistance of silicate coatings can be attributed to additional penetration of $[\text{BO}_4]^{5-}$ complexes into the vitreous phase of enamel as a consequence of its reaction with the borated surface of metal in the course of coating formation.

Thus, bismuth-bearing powder material – silicate coating composites have enhanced service characteristics, higher atmospheric and corrosion resistance, and hardness than powder materials without a coating. Moreover, the composites

have sufficiently high parameters of coating quality, impact strength, and adhesion strength, due to using the proposed method of preliminary borating of material and a special bismuth additive to powder steel. All this suggests that silicate coatings are promising for use in machine building to impart special service properties to powder materials.

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